

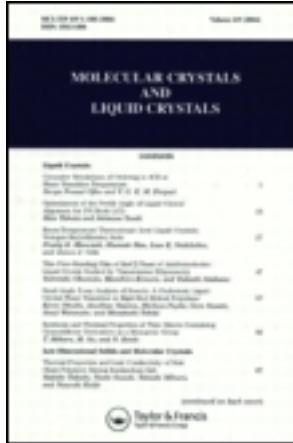
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PHOTOVOLTAIC CHARACTERISTICS OF BORON DOPED AMORPHOUS CARBON FILMS DEPOSITED BY PULSED LASER DEPOSITION USING GRAPHITE TARGET

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This paper reports on the successful deposition of boron (B) doped carbon films (p-C(B)) and fabrication of p-C(B)/n-Si solar cells by pulsed laser deposition (PLD) technique at room temperature using graphite target. The B content in the film was determined by X-ray photoelectron spectroscopy (XPS) to be in the range of 0.2–1.7 atomic percentage. The photovoltaic values of the device, a maximum open circuit voltage, $V_{oc} = 250\text{ mV}$ and short circuit current density, $J_{sc} = 2.113\text{ mA/cm}^2$ were obtained, when exposed to AM 1.5 illumination (100 mW/cm^2 , 25°C). The maximum energy conversion efficiency was found tentatively to be about, $\eta = 0.2\%$, together with the fill factor, $FF = 45\%$. In this paper, the dependence of the B content on electrical and optical properties of the p-C(B) films and the photovoltaic characteristic of the p-C(B)/n-Si structure photovoltaic solar cells are discussed.

Keywords: photovoltaic; solar cell; heterojunction; boron doping; pulsed laser deposition; graphite target; amorphous carbon

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INTRODUCTION

It is imperative to find a new kind of clean and cheap energy resource in the 21st century. In the search for alternative materials, carbon – a group IV element existing in many forms with a wide range of optoelectrical properties is highly attractive for its possible application in optoelectric devices such as photovoltaic solar cells. Amorphous carbon (a-C) shows semiconducting nature, which promotes its application in the field of semiconductor technology, such as fabrication of photovoltaic solar cells.

However, undoped carbon is to be slightly p-type and when we attempt to utilize such carbon as alternative material in optoelectronic devices, control of the conduction type of a carbon film is indispensable. Boron (B) is widely used as p-type impurity in silicon (Si) semiconductor. Recently, it has been reported that B can also be used as p-type dopant of carbon film, using chemical vapor deposition and ion implantation techniques [1,2].

However, as far as we know, the electronic B doping into carbon film is not yet realized by pulsed laser deposition (PLD) technique using a conventional graphite target. In our experiment, B doped p-type carbon (p-C(B)) films were successfully obtained by XeCl excimer laser using a graphite target at room temperature. The measurements on current-voltage (I-V) characteristics under dark and AM 1.5 illumination conditions are conducted in this work. In this paper, the optoelectrical properties and photovoltaic characteristics of the B doped carbon films based solar cells are reported.

EXPERIMENTAL

The p-C(B) films were prepared on single crystalline n-type Si (100), p-C(B)/n-Si and quartz substrates by excimer laser (NISSIN 10X, XeCl, $\lambda = 308$ nm, $\tau = 20$ nsec, repetition rate = 5 Hz, spot size = 5.5 mm²), which is focused on the target at an incident angle of 45° to the target normal. In order to dope, target was prepared by mixing the powder of pure graphite with varying amount of B powder (1 to 20% by weight) and compressed into pellets. Before deposition, the substrates were cleaned with acetone and methanol in a hot water bath at 55°C for 5 minutes. After cleaning, they were etched with HF:H₂O (1:10) in order to remove the resistive native oxide formed over the surface, and quickly transferred into the PLD chamber. The films were deposited at room temperature at a base pressure of $\sim 2 \times 10^{-5}$ Torr and the laser energy was 150 mJ/pulse on the window of PLD chamber.

The thickness of the p-C(B) films was measured by DEKTAK profilometer to be approximately 60 nm on the n-Si substrates, and 100 nm on the

quartz substrates. The front side (p-C(B) films) and back side (n-Si) contacts of the cells were made with gold (Au) electrode by depositing a transparent Au films of thickness 10 nm on top of the p-C(B) films and a relatively thick films of Au-Sb/Au films of thickness 18/100 nm at the bottom of the n-Si substrates, using a conventional vacuum/electron beam evaporation system. The contacts, Au electrodes to the p-C(B) films and Au-Sb/Au electrodes to the n-Si substrates, all showed ohmic characteristics, served as an active area for the cells of the above configuration. Upon illumination under AM 1.5 SUN condition, the cells reveal the photovoltaic characteristics that will be discussed below. All the films and cells were analyzed by using standard experimental characterization techniques.

RESULTS AND DISCUSSIONS

1. Film Compositions

The atomic (at.) percentage (%) of B in the carbon films (BCF) was determined by X-ray photoelectron spectroscopic (XPS) analyses. The instrument used was SSX-100 XPS system of Surface Science Instruments utilizing $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) radiation, under high vacuum condition of about 10^{-10} Torr. Figure 1 shows the variation of the at. % of BCF as a

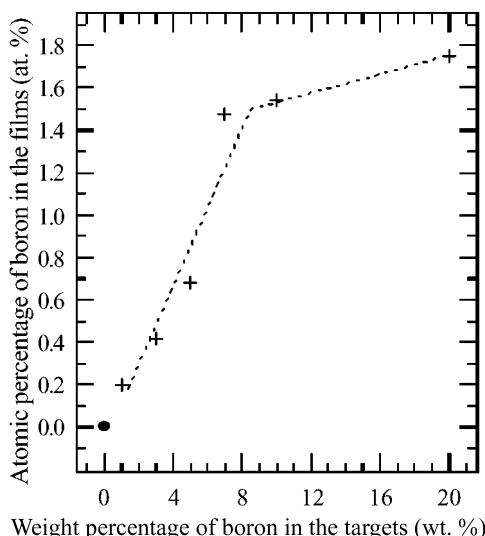


FIGURE 1 The variation of atomic percentage of boron in the films as a function of weight percentage of boron in the targets.

function of weight % (wt. %) of B in the target (BT). The at. % of BCF is found to be approximately proportional linearly up to 7 wt. % of BT, after which it gradually increases, tends to a constant nearly to about 1.75 at. % of BCF, suggesting saturation of B content.

The at. % of BCF is much lower than that wt. % of BT. It is believed to relate this phenomenon to the low ablation rate of the B at the laser wavelength of 308 nm, which agree with the mechanism of ablation of PLD that has been described by T. Jeffrey *et al.* [3].

2. Optical and Electrical Properties

Figure 2 shows a plot of optical absorption coefficient (α) of the films as a function of wavelength, obtained from optical transmittance and reflectance measurements in the range of 200 to 2000 nm to derive the Tauc optical gap (E_g) for amorphous semiconductors. The α of the films indicates in the order of $10^4 \sim 10^5 \text{ cm}^{-1}$ for the measured photon energy range from 1 to 4 eV.

The films have high α and have very broad absorption edge owing to the typical characteristic of amorphous nature of carbon materials. The high α in the power-law (Tauc) and exponential (Urbach) region is ascribed to the presence of more graphitic component trihedral (sp^2) in the p-C(B) films with the decrease of BT.

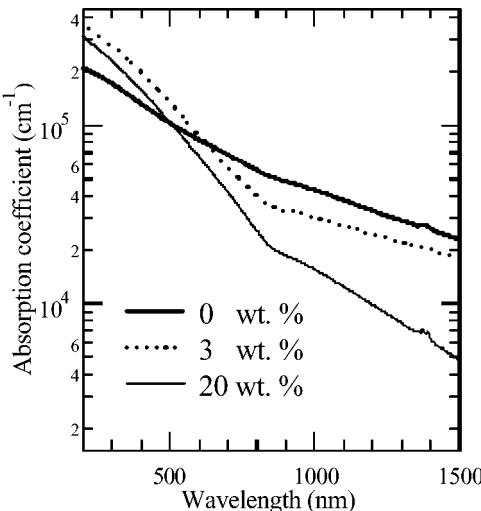


FIGURE 2 The absorption coefficient of the carbon films as a function of wavelength.

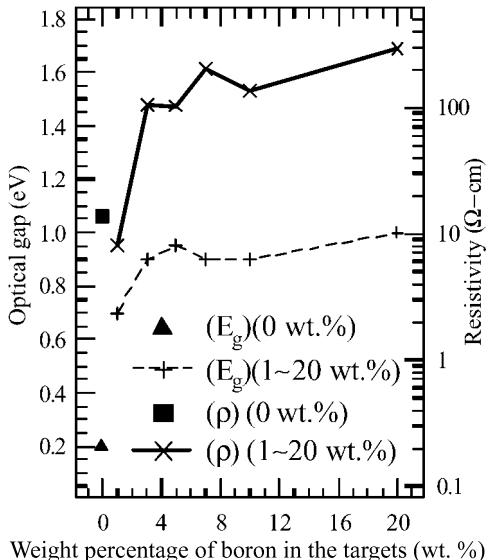


FIGURE 3 The variation of resistivity and optical gap as a function of weight percentage of boron in the targets.

The E_g of the films is obtained from the extrapolation of the linear part of the curve at the $\alpha=0$, using the Tauc relation [4]. The E_g is found to increase with the increasing of B content in the B doped carbon films. The estimated E_g of undoped carbon film (0 wt. % of BT) is approximately 0.2 eV, while the films deposited from the target containing 3 and 5 wt. % of BT, increase to 0.9 and 1.0 eV, respectively (Fig. 3). The increase of E_g is perhaps due to the increase of the tetrahedral (sp^3) hybrids forms of carbon and B induced disorder of the structure [5].

The electrical resistivity (ρ) of the films is measured by 4-probe method at room temperature. The ρ is seen to vary with WBT, decreases initially with addition of a small amount of B at 1 wt. % of BT and then increases with the increase of wt. % of BT (Fig. 3).

The behavior of E_g and ρ is different from the results observed by W. Chan *et al.* [6], which found that the both E_g and ρ decreased with increasing B concentration in reliable B doping. Thus, the doping efficiency of B is lower in our experiment and may also probably due to the heavy doping [7].

3. Characteristics of Photovoltaic Solar Cells

Photovoltaic solar cells of configurations p-C(B)/n-Si has been fabricated. From the I-V measurement, the I-V characteristics of the p-C(B)/n-Si

configuration photovoltaic solar cells, without light irradiation, displayed a rectifying I-V characteristic. Upon illumination under AM 1.5 SUN condition, the p-C(B)/n-Si structure shows rectifying characteristic, indicating the formation of heterojunction between the B doped carbon films and Si substrates.

In the dark, without light irradiation, the I-V characteristics of the p-C(B)/n-Si photovoltaic solar cells show better rectifying characteristics (ideality factor n : 1.6–1.8) in a light doping region of lower wt. % of BT (target containing 1 and 3 wt. % of BT), and upon illumination under AM 1.5 illumination (100 mW/cm^2 , 25°C) condition, the I-V characteristics of the p-C(B)/n-Si photovoltaic solar cells show higher open circuit voltage and short circuit current compared to a heavy doping region of higher wt.% of BT (target containing more than 3 wt. % of BT).

Figure 4 shows the I-V characteristics of the photovoltaic solar cells deposited from the target containing 3 wt. % of BT. The open circuit voltage, $V_{oc} = 250 \text{ mV}$, the short circuit current, $I_{sc} = 0.845 \text{ mA}$, and the short circuit current density, $J_{sc} = 2.113 \text{ mA/cm}^2$ was obtained (The area of the cells is approximately 0.4 cm^2). According to calculation, under AM 1.5 illumination (100 mW/cm^2 , 25°C), the maximum power (P_{max}), the energy conversion efficiency (η) and the fill factor (FF) of the photovoltaic solar cells were about 0.093 mW , 0.2% and 46% , respectively.

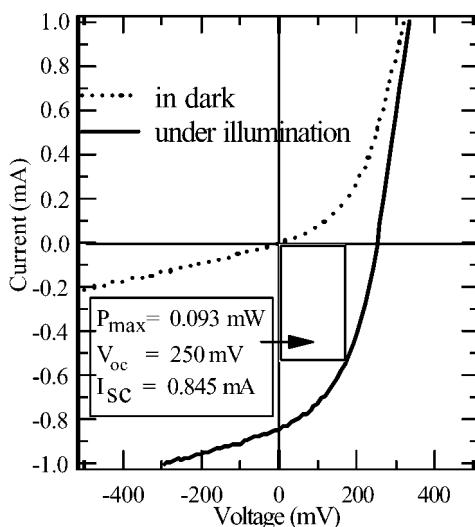


FIGURE 4 The I-V characteristics of the p-C(B)/n-Si junction solar cell in dark and under illumination (Target: 3 wt. %).

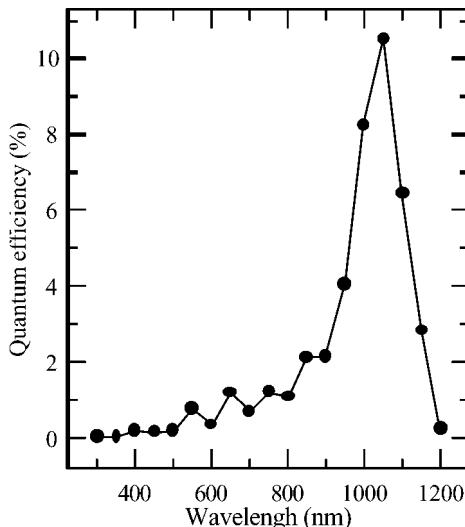


FIGURE 5 The spectral responses of the p-C(B)/n-Si junction solar cell (Target: 3 wt. %).

Figure 5 shows the quantum efficiency (QE) of the photovoltaic solar cells from the target containing 3 wt. % of BT. A low efficiency is found in the wavelength region of 300~800 nm, and a spectral response peak of approximately 10% is shown at 1050 nm in the wavelength region of 900~1200 nm.

The value of QE in the short wavelength is as low as that reported by K. L. Narayanan *et al.* [8], but much higher than their results in the long wavelength region. Both the Au electrode films and the B doped carbon films (3 wt. % of BT) have higher absorption coefficients of $2.4 \times 10^5 \sim 5.3 \times 10^5$ and $4.1 \times 10^4 \sim 3.6 \times 10^5 \text{ cm}^{-1}$, respectively [8]. We think that the high absorption coefficients of Au electrodes and the B doped carbon films in short wavelength region are responsible to the low QE.

The spectral response shown in the long wavelength region is similar to that of single-crystal solar cells. Generally, in the long wavelength region, the spectral response of a photovoltaic solar cells primarily depends on the optical absorption properties of the substrates of a photovoltaic solar cells [9].

When the light is incident on the front of surface (p-C(B) films), the photon in the short wavelength is strongly absorbed by the Au electrodes and B doped carbon films, and most part of generated electron-hole pairs recombined in the surface and only a few of them can arrive at depletion

region. Therefore, the B doped carbon films have a few contribution to QE of the p-C(B)/n-Si photovoltaic solar cells.

Based on spectrum response analyses, we concluded that when we use p-C(B) films as a window of a photovoltaic solar cells, the high absorption of the Au electrodes and B doped carbon films would be the major reason for the low η .

CONCLUSIONS

In summary, according to our knowledge, it is the first time that the B species have been successfully incorporated into the a-C films. In our experiment, p-type carbon films were prepared by PLD from graphite with B doping. The I-V curves of the p-C(B)/n-Si photovoltaic solar cells in dark and under illuminated conditions are given in the paper. The B doping does not only significantly increases the E_g by increase of sp^3 , but also improved the η of photovoltaic solar cells behavior. The maximum η of the photovoltaic solar cells constructed by p-C(B) films and n-Si substrates was 0.2%.

Although the η is still low, it has shown that there is the possibility of the improvement of the η of the p-C(B)/n-Si photovoltaic solar cells by optimizing the deposition conditions. These results would encourage the future prospects of clean, low-cost and reasonably high efficiency carbon solar cells. Further studies on the junction properties of p-C(B)/n-Si structures are in progress.

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